

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
26 July 2001 (26.07.2001)

PCT

(10) International Publication Number
WO 01/53565 A1

- (51) International Patent Classification⁷: C23C 16/34
- (21) International Application Number: PCT/KR01/00107
- (22) International Filing Date: 22 January 2001 (22.01.2001)
- (25) Filing Language: Korean
- (26) Publication Language: English
- (30) Priority Data:
2000/2958 21 January 2000 (21.01.2000) KR
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- (81) Designated States (national): DE, JP, KR, US.
- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 01/53565 A1

(54) Title: PROCESS FOR PREPARING METAL NITRIDE THIN FILM EMPLOYING AMINE-ADDUCT SINGLE-SOURCE PRECURSOR

(57) Abstract: The present invention relates to a process for preparing metal nitride thin film by chemical deposition employing amine-adduct single-source precursor at low temperatures. In accordance with the present invention, the chemical deposition is performed at low temperatures with a relatively cheap silicon substrate instead of expensive sapphire, which makes possible the economical preparation of the nitride thin film. Furthermore, since the invented process can eliminate the problems confronted in the post electrode deposition caused by insulating substrate, it can be practically applied to the development of new materials and the preparation of multi-layer thin film.

**PROCESS FOR PREPARING METAL NITRIDE THIN FILM EMPLOYING
AMINE-ADDUCT SINGLE-SOURCE PRECURSOR**

5 BACKGROUND OF THE INVENTION

Field of the Invention

10 The present invention relates to a process for preparing metal nitride thin film employing amine-adduct single-source precursor, more specifically, to a process for preparing metal nitride thin film by chemical vapor deposition employing amine-adduct single-source precursor at low temperatures.

15

Background of the Invention

20 The compound semiconductors of gallium nitride(GaN), aluminum nitride(AlN), and indium nitride(InN) are excellent materials for bandgap engineering, because they form a continuous range of solid solutions and superlattices with direct room-temperature band gaps ranging from 1.9eV for InN, to 3.4eV for GaN, to 6.2eV for AlN. Recently a great deal of interest has been shown especially in the $\text{In}_x\text{Ga}_{1-x}\text{N}$ due to its worldwide demand for high-brightness blue and green light-emitting diodes(LEDs) and laser diodes(LDs)(see: S. Nakamura et al., Appl. Phys. Lett., 64:1687, 1994).

30 The group III nitride semiconductor thin film has been mainly prepared by chemical vapor deposition(CVD) routes involving the reaction of either a metal halide or metal alkyl with ammonia as a nitrogen source(separate source CVD). Although significant progress has been made, a major process limitation still exists in that the high thermal stability of ammonia still necessitates the use of
35 very high substrate temperatures(typically in excess of 900°C), which leads to high concentrations of nitrogen

vacancies (and hence high n-type background doping levels) in the deposited material, even when V/III ratios as high as 2000:1 are used. Therefore, ammonia-based CVD reactions are severely limited by the nitride material p-doping capability arising from the presence of the n-type nitrogen vacancies, the highly inefficient use of toxic ammonia gas, and the resulting requirement to install expensive exhaust-gas scrubbing systems. Besides, when grown to the multi-layer thin film, thermally unstable films cannot be deposited on the same substrate because the interlayer diffusion occurs more rapidly at a high temperature. Secondly, it is difficult to control the chemical composition of thin film because more than two precursors with different vapor pressures are used. Thirdly, trimethylmetal and ammonia used as the thin film precursors are difficult to deal with due to their high reactivity and toxicity (see: S. Stride and H. Morko, *J. Vac. Sci. Technol.*, 10:1237, 1992).

To overcome these problems, alternative group 13-nitrogen single-source precursors are now being investigated in an effort to achieve group III nitride growth at significantly lower temperatures and V/III ratios. Single-source precursors, containing both the metal and nitrogen atoms which will combine to form the metal nitride, can offer several advantages over the separate source CVD routes: First, if the correct stoichiometric ratio of M to N is possessed by the precursor, then this ratio can be retained in the metal nitride thin film produced from the precursor; therefore the facile formation of the thin film with exact composition is possible. Secondly, chemical bonds between metal and nitride already exist so that the surface diffusion and the activation energy for the bond formation among the elements on the surface of the substrate are not much required. Thirdly, single-source precursors have very low reactivity and toxicity, and are easy to deal with and to purify by recrystallization or sublimation. In addition,

the deposition temperature of the thin film is relatively low to make it possible to use thermally unstable materials as substrates and to prevent interlayer diffusion. As examples, a single-source precursor
5 [(Me₂N)(N₃)Ga(μ-NMe₂)]₂ has been used to prepare a gallium nitride thin film at 580°C (see: D. A. Neumayer et al., *J. Am. Chem. Soc.*, 117:5893, 1995) and another single-source precursor [(N₃)₂Ga(CH₂CH₂CH₂NMe₂)] has been used for the preparation of a gallium nitride thin film at 750°C (see: R.
10 A. Fischer et al., *J. Cryst. Growth*, 170:139, 1997).

However, even though the thin films described above are prepared at lower temperatures than that of prior art, the interlayer diffusion and the decrease in quality due to the vapor pressure decrease and the precursor
15 decomposition are still to be solved. Besides, the unit cost of production is relatively high because sapphire is used as the substrate for the thin film deposition.

Therefore, there are strong reasons for developing a process for preparing a thin film at lower temperatures in
20 an economical manner, while overcoming the interlayer diffusion and the quality decrease of the thin film.

SUMMARY OF INVENTION

25 The present inventors have made an effort to develop an economical process for preparing a thin film at lower temperature to overcome the interlayer diffusion and the quality decrease of the thin film, and discovered that metal nitride thin films can be prepared by the deposition
30 of XIII group metal nitride compounds including gallium nitride onto a silicon substrate using amine-adduct precursors of R₂(N₃)M:D.

A primary object of the present invention is,
35 therefore, to provide a process for preparing metal nitride thin films employing amine-adduct single-source

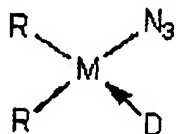
precursors.

The other object of the present invention is to provide metal nitride thin films prepared by the process..

5 DETAILED DESCRIPTION OF THE INVENTION

The crystal structure of a multi-layer thin film is generally known to depend on the types and orientation of substrate used. To obtain hexagonal gallium nitride thin
10 films has been usually used sapphire as the substrate, especially with the c-faced crystal structure, since the sapphire is stable at a high temperature, easy to pre-treatment, and has a hexagonal symmetry. On the other hand, the use of silicon substrate makes sure that, compared to
15 insulating sapphire, the post electrode formation is facilitated, the change of the substrate to have a larger diameter is possible, and the final elements are easily separated.

20 The process for preparing metal nitride thin films employing amine-adduct single-source precursors of the present invention comprises the steps of: placing an amine-adduct single-source precursor(I) onto a substrate, heating at 350 to 400°C under a pressure of 0.5×10^{-7} Torr
25 and vaporizing the amine-adduct single-source precursor(I); controlling the vapor pressure of the single-source precursor from 1.0×10^{-6} to 3.0×10^{-6} Torr followed by chemical deposition for 1.5 to 2.0 hours to form a buffer layer; and, subsequent chemical deposition
30 for 12 to 24 hours under a pressure of 1.0×10^{-6} to 3.0×10^{-6} Torr to prepare a metal nitride thin film.



(I)

wherein,

D represents NH_3 , NH_2R , or NH_2NR_2 ;

M represents Al, Ga, or In; and,

R represents H, Me, Et, *n*-Pr, *i*-Pr, *t*-Bu, Cl,
or Br.

The process for preparing of metal nitride thin films by the chemical deposition at low temperatures is illustrated in more details by the following steps.

Step 1: Vaporization of single-source precursor

An amine-adduct single-source precursor(I) is placed onto a substrate, heated at 350 to 400°C under a pressure of 0.5×10^{-7} to 1.5×10^{-7} Torr, and subsequently vaporized, where silicon, sapphire, and SiC may be preferably used as the substrate, though silicon is the most preferred. The temperature of the substrate is measured using an optical thermometer or calculated from the amount of current using a correction diagram showing the correlation between temperature and current passing through the silicon substrate.

Step 2: Formation of buffer layer

A buffer layer is formed by controlling the vapor pressure from 1.0×10^{-6} to 3.0×10^{-6} Torr followed by chemical deposition for 1.5 to 2.0 hours, where the buffer layer may be formed to contain GaN or AlN depending on the amine-adduct single-source precursor employed in the process.

Step 3: Preparation of metal nitride thin film

A metal nitride thin film is prepared by the chemical deposition of the buffer layer for 12 to 24 hours under a pressure of 1.0×10^{-6} to 3.0×10^{-6} Torr, where the thin

film preferably contains a mixture of AlN, GaN, InN, AlGaIn, GaInN, AlInN, and AlGaInN. The equipment for chemical deposition of the metal nitride is not limited to special types, however, a high vacuum (10^{-7} Torr) chemical deposition apparatus with an oil diffusion pump and liquid nitrogen traps is preferred. The high vacuum apparatus is shaped in a jointed cold wall with the copper gasket, and equipped with a flange made of stainless steel pipe and high vacuum valves to control the pressure of sample tube and precursor.

The present invention is further illustrated by the following examples, which should not be taken to limit the scope of the invention.

Example 1: Preparation of $\text{Et}_2(\text{N}_3)\text{Ga}:\text{NH}_3$

0.88g $[\text{Et}_2\text{Ga}(-\mu\text{-NH}_2)]_3$ was dissolved in Et_2O , and 0.26g hydrogen azide was added dropwise at -60°C with stirring. The reaction temperature was warmed to room temperature and the solution was stirred for 2 hours. After the completion of the reaction, the solvent was removed in vacuo to give 0.91g of colorless liquid, which was then purified by distillation to yield $\text{Et}_2(\text{N}_3)\text{Ga}:\text{NH}_3$ with a melting point of -10°C .

^1H NMR (CDCl_3 , 20°C): δ 0.56 (q, Ga- CH_2CH_3), 1.12 (t, Ga- CH_2CH_3), 3.05 (s, N-H);

^{13}C NMR (CDCl_3 , 20°C): δ 2.80 (Ga- CH_2CH_3), 9.24 (Ga- CH_2CH_3);

MS (70eV): m/z 140 ($\text{M}^+ - [\text{Et} + \text{NH}_3]$);

IR (N_3): $2073, 2254\text{cm}^{-1}$.

Example 2: Preparation of metal nitride thin film using $\text{Et}_2(\text{N}_3)\text{Ga}:\text{NH}_3(\text{I})$

0.1g $\text{Et}_2(\text{N}_3)\text{Ga}:\text{NH}_3$ was placed in a container,

silicon(111) wafer was heated at 350°C under the initial pressure of 1.0×10^{-7} Torr, and the total pressure was adjusted to 3.0×10^{-5} Torr by controlling the vapor pressure of $\text{Et}_2(\text{N}_3)\text{Ga}:\text{NH}_3$ with metering valve, and then
5 chemical vapor deposition was performed for 1.5 hour. The deposited metal gallium nitride thin film was blue-colored and 0.15 μm thick, which was confirmed by the SEM photographs of fractured sections. The X-ray diffraction analysis showed the formation of a polycrystalline GaN
10 buffer layer. The reactor pressure was increased to 6.0×10^{-6} Torr followed by chemical deposition for 12 hours to yield a black gallium nitride thin film. The SEM photographs of fractured sections revealed that the film has a thickness of 2 μm , and the deposition rate was
15 0.15 $\mu\text{m/hr}$. Rutherford backscattering spectrometry(RBS) analysis showed that the thin film was consisted of 1:1 stoichiometric ratio of gallium and nitrogen. A gallium nitride(002) peak was observed at 34.5° when X-ray diffraction analysis of the thin film was performed with
20 changing 2θ from 20° to 80°. Pole figure analysis also confirmed that the thin film has grown to the hexagonal structure. The formation of the polycrystalline buffer layer was confirmed by analyzing the TEM image, and electron diffraction analysis confirmed that the formation
25 of gallium nitride growth as columnar structure on the buffer layer.

Example 3: Preparation of metal nitride thin film
employing $\text{Et}_2(\text{N}_3)\text{Ga}:\text{NH}_3(\text{II})$

30

A metal nitride thin film was prepared in an analogous manners as in Example 2, except that the silicon wafer was heated at a temperature of 400°C. As the result, a black gallium nitride was prepared with a thickness of
35 2.2 μm and the deposition rate of 0.16 $\mu\text{m/hr}$, which was measured by the SEM photographs of fractured sections. The

other characteristics of the deposited thin film were identical to the thin film prepared in Example 2.

As clearly described and demonstrated as above, the
5 present invention provides a process for preparing metal
nitride thin films by chemical deposition at low
temperatures employing amine-adduct single-source
precursors. In accordance with the present invention, the
chemical deposition is performed at low temperatures with
10 a relatively cheap silicon substrate instead of expensive
sapphire, which makes it possible the economical
preparation of the nitride thin film. Furthermore, since
the substrate is silicon semiconductor instead of sapphire
insulator, the electrode can be easily formed on the
15 backside of the substrate.

Although the preferred embodiments of present
invention have been disclosed for illustrative purpose,
those who are skilled in the art will appreciate that
20 various modifications, additions, and substitutions are
possible, without departing from the spirit and scope of
the invention as disclosed in the accompanying claims.

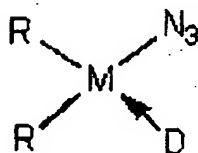
WHAT IS CLAIMED IS:

1. A process for preparing metal nitride thin film
employing amine-adduct single-source precursor which
5 comprises the steps of:

(i) placing an amine-adduct single-source
precursor(I) onto a substrate, heating at 350 to 400°C
under a pressure of 0.5×10^{-7} Torr and vaporizing the
amine-adduct single-source precursor(I);

10 (ii) controlling the vapor pressure of the single-
source precursor from 1.0×10^{-6} to 3.0×10^{-6} Torr followed
by chemical deposition for 1.5 to 2.0 hours to form a
buffer layer; and,

(iii) chemical deposition for 12 to 24 hours under
15 a pressure of 1.0×10^{-6} to 3.0×10^{-6} Torr to prepare a
metal nitride thin film



20 wherein,

D represents NH_3 , NH_2R , or NH_2NR_2 ;

M represents Al, Ga, or In; and,

R represents H, Me, Et, *n*-Pr, *i*-Pr, *t*-bu, Cl,
or Br.

25

2. The process for preparing metal nitride thin film
employing amine-adduct single-source precursor of claim 1,
wherein the substrate is silicon, sapphire or SiC.

30 3. The process for preparing metal nitride thin film
employing amine-adduct single-source precursor of claim 1,
wherein the buffer layer contains GaN or AlN.

4. The process for preparing metal nitride thin film

employing amine-adduct single-source precursor of claim 1, wherein the metal nitride thin film contains a mixture of AlN, GaN, InN, AlGaIn, GaInN and AlInN.

- 5 5. A metal nitride thin film prepared by the process of claim 1 which is chemically deposited on a silicon substrate.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR01/00107

A. CLASSIFICATION OF SUBJECT MATTER**IPC7 C23C 16/34**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C23C 16/34, 16/00: C07F 7/00, 7/02, 7/28: H01L 21/3205, 21/205

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Patents and Applications for Inventions since 1970

Korean Utility Models and Applications for Utility Models since 1970

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,194,642 A(WINTER et al.) 16 MAR. 1993, column 2, line 45 - column 3, line 48	1-5
A	US 5,591,483 A(WINTER et al.) 7 JAN. 1997, see the entire document	1-5
A	US 5,344,948 A(VERKADE) 6 SEPT. 1994, see the entire document	1-5
A	JP 6-61,229 A(FUJITSU LTD. AND TOKYO ELECTRON LTD.), see the entire document	1-5

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

07 MAY 2001 (07.05.2001)

Date of mailing of the international search report

08 MAY 2001 (08.05.2001)

Name and mailing address of the ISA/KR

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